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Ultraviolet Photoionization Efficiency of the Vaporized Ionic Liquid 1-Butyl-3-methylimidazolium Tricyanomethanide: Direct Detection of the Intact Ion Pair

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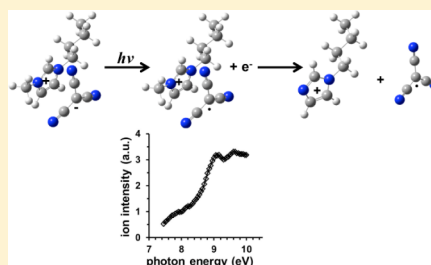
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ABSTRACT: We present the first direct measurement of a neutral, intact ion pair photoionization efficiency (PIE) curve for a vaporized ionic liquid, 1-butyl-3-methylimidazolium tricyanomethanide, using tunable vacuum ultraviolet (VUV) photoionization time-of-flight mass spectrometry (PI-TOFMS). The ionization potential (IP) for the ion pair is experimentally determined to be 6.6 ± 0.5 eV, which matches reasonably well with the adiabatic IP of 7.3 ± 0.2 eV calculated at the M06/6-31+G(d,p) level of theory. The lifetime to dissociation of the cation–radical complex formed upon ionization of the ion pair is highly dependent upon entropic contributions. Thermal gravimetric analyses (TGA) determined the enthalpy of vaporization to be $\Delta H_{\text{vap}}(298 \text{ K}) = 143.5 \pm 6.2$ kJ/mol and that vaporization of BMIM⁺TCM[−] as ion pairs is the dominant mechanism for mass loss under the experimental conditions for VUV PI-TOFMS ($T = 433 \text{ K}$).

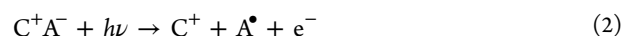
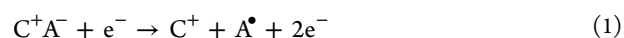
SECTION: Spectroscopy, Photochemistry, and Excited States



Although room-temperature molten salts, more recently known as ionic liquids (ILs), have been known for almost a century (for example, ethylammonium nitrate, MP = 12 °C, was discovered in 1914),¹ the rapid development of IL chemistry has only occurred within the past decade. In 2000, only 217 papers were published on the subject, whereas in 2010, over 6000 papers were published [SciFinder results searching for the concept “ionic liquid” (August 2011)]. The major interests in ILs are due to such properties as (1) extremely low vapor pressures, making ILs suitable for volatile organic compound (VOC) solvent replacements, (2) thermal stability (nonflammability), (3) high conductivity (suitable for electrochemistry and fuel cells), and (4) high energy density (suitable as “green” propellants²). The number of possible ILs has been estimated at $10^{18.3}$. ILs are based on cations such as, but not limited to, ammonium, imidazolium, triazolium, tetrazolium, and phosphonium ions. Common anions include the halide, nitrate, dicyanamide, bistrifluoromethylsulfonylimide, and sulfonate ions. The popular assumption that ILs exert no vapor pressure was disproved when certain classes of ILs were shown to distill in vacuum and the material recovered was identical to the starting material.⁴ However, the vaporization mechanism of a distilling IL has been somewhat controversial. Many ILs have activation barriers to thermal decomposition that can be comparable to or below the enthalpy of vaporization of the IL, so that decomposition competes with

or dominates over vaporization.^{5–7} The question has arisen that upon vaporization, do the ILs, which exist as discrete ions in the liquid, vaporize as individual ions, as neutral ion pairs, or as neutral or charged ion clusters?

It has been shown that the most acidic proton on the cation largely determines the IL's thermal stability.⁸ When hydrogens are attached to the cationic nitrogens, they are more acidic, and those ILs have been termed “protic” ILs.⁹ In general, protic ILs have lower thermal stability than ILs with alkyl substituents on the ring nitrogens, known as “aprotic” ILs. Vaporization of protic ILs occurs via proton transfer from the cation to the anion, and the resulting neutral species formed can then evaporate.⁹ Recent mass spectrometric experiments indicate the vaporization of many aprotic ILs under vacuum distillation conditions proceeds via neutral cation–anion pairs, which is evidenced by the dissociative ionization (DI) of the ion pair and subsequent detection of the resulting cation.^{10,11}

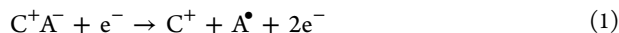


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A similar mechanism has been proposed for dication-based ILs.¹² Ion cyclotron resonance experiments indicate vaporization of intact ion pairs from the detection of the cation upon injection of ionizing electrons and the further formation of charged clusters.^{9,13}



Selected ion flow tube (SIFT) experiments indicate vaporization of intact ion pairs by attachment of a third ion, $\text{C}_1^+\text{A}^- + \text{C}_2^+ \rightarrow \text{C}_1^+\text{A}^-\text{C}_2^+$.¹⁴ Matrix isolation FTIR experiments have been able to identify the structure of ion pairs frozen in a rare gas matrix.¹⁵ Due to the large UV photoabsorption cross section of the ion pair, UV measurements under vacuum distillation conditions have been able to accurately determine the values for the enthalpy of vaporization.¹⁶ Theory has shown that the formation of single ion pairs is energetically favored over the formation of separate ions or clusters.¹⁷ Gas-phase ion pairs of vaporized 1-butyl-3-methylimidazolium tricyanomethanide ($[\text{BMIM}]^+[\text{C}(\text{CN})_3]^-$ or $\text{BMIM}^+\text{TCM}^-$) have been previously detected directly by pulsed field ionization mass spectrometry¹⁸ at temperatures near or above the thermal decomposition onset temperature of the IL, presumably as vaporization still competes with thermal decomposition at these temperatures for this IL. It should be noted that $\text{BMIM}^+\text{TCM}^-$ was the first IL discovered to be enriched upon fractional distillation of IL mixtures,¹⁸ and it has one of the lowest reported values for the enthalpy of vaporization for ILs, $\Delta H_{\text{vap}}(298 \text{ K}) = 143.2 \pm 5 \text{ kJ/mol}$.¹⁹

In this Letter, we present the direct detection of intact ion pairs from the vaporized IL $\text{BMIM}^+\text{TCM}^-$ by soft VUV photoionization, as well as the first measured PIE curve of a vaporized IL ion pair. This experimental breakthrough was possible due to the combination of high ion pair number density (by locating the effusive IL source as close as possible to the ionization region, Figure 1) and the high sensitivity afforded

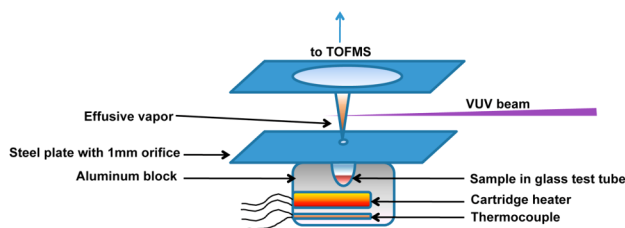


Figure 1. Effusive IL source.

by the synchrotron VUV light source. Thermal gravimetric analyses (TGAs) reveal that the vaporization of the IL will be the dominant mass loss process in the photoionization experiments. Once the ion pair is vaporized and subsequently ionized, even though entropy favors the dissociation of the cation–radical complex, the lifetime of the ionized ion pair is sufficiently long to measure the PIE curve of the intact ion pair.

The nonisothermal gravimetric analysis of $\text{BMIM}^+\text{TCM}^-$ in Figure 2a reveals the onset temperature to be $\sim 513 \text{ K}$ as determined by the onset of the nonzero slope. The mass loss rate due to thermal decomposition in nonisothermal gravimetric analysis is highly dependent upon the sample heating rate, where high heating rates strongly favor thermal decomposition over vaporization.²⁰ Figure 2b is an Arrhenius-type plot of the mass loss rate versus $1/T$, whose slope is equal

to $-\Delta H/R$, where the phenomenological activation enthalpy for decomposition is $\Delta H = 183.0 \pm 4.3 \text{ kJ/mol}$ at an average temperature of 582 K and the reported error is twice the standard deviation ($\pm 2\sigma$). Isothermal gravimetric analysis to determine the enthalpy of vaporization, ΔH_{vap} , of the IL²¹ is shown in Figure 2c and d, where ΔH_{vap} is determined to be $126.0 \pm 6.2 \text{ kJ/mol}$ (where the error is $\pm 2\sigma$) at an average temperature of 473 K . Using a $\Delta_g^1\text{C}_{\text{pm}}^\circ$ value of 100 J/mol-K ¹⁹ for the change in molar heat capacity upon vaporization, the corrected ΔH_{vap} at 298 K is $143.5 \pm 6.2 \text{ kJ/mol}$, in excellent agreement with a previously reported value of $143.2 \pm 5.0 \text{ kJ/mol}$.¹⁹ By extrapolating the total and vaporization mass loss rates in Figure 2b and d to 433 K , the mass loss contributions from vaporization and thermal decomposition are estimated to be 6.0×10^{-7} and $2.5 \times 10^{-9} \text{ mg/s}$, respectively, indicating that vaporization is approximately 240 times faster than thermal decomposition at 433 K .

Photoionization mass spectra at a photon energy of 7.50 eV for $\text{BMIM}^+\text{TCM}^-$ is shown in Figure 3a. Figure 3b clearly shows the ion pair at $m/z = 229$, and Figure 3c shows the cation formation at $m/z = 139$ from DI of the ion pair, and the corresponding ^{13}C peaks are visible at $m/z = 230$ (15%) and 140 (9.6%), respectively. No cluster formation at higher masses is detected up to $m/z = 600$. Figure 4a and b shows the photoionization efficiency (PIE) curve for the ion pair ($m/z = 229$). In Figure 4b, the PIE curve is fit using a functional form $\alpha(E - E_0)^2$ using a least-squares analysis, where α is a normalization factor, E is the photon energy, and E_0 is the ionization potential (IP) to be fit.²² This analysis yields an IP of $6.6 \pm 0.5 \text{ eV}$, which matches reasonably well with the M06-calculated adiabatic IP of $7.3 \pm 0.2 \text{ eV}$. The BMIM^+ cation formed upon DI of the ion pair has an appearance energy (AE), determined similarly to the IP above, of $6.9 \pm 0.5 \text{ eV}$, with a calculated value of $6.9 \pm 0.2 \text{ eV}$ at the M06/6-31+G(d,p) level of theory. The larger uncertainty of $\pm 0.5 \text{ eV}$ associated with the experimental IP and AE values below 7.4 eV is due to the need to extrapolate the IP from the PIE data, which are only measured above 7.4 eV (7.4 eV being the lower limit of the synchrotron undulator output). It is possible that thermal contributions to the internal energy of the evaporated ion pair can contribute to the available energy for ionization and fragmentation, thereby shifting the experimental IPs and AEs to lower energies.²² Considering the 90 vibrational degrees of freedom in $\text{BMIM}^+\text{TCM}^-$, a shift to lower energy of up to 0.5 eV is possible if all of the thermal energy, $\Delta U = 1/2Nk\Delta T$, where N is the number of vibrational degrees of freedom in the molecule, is available for ionization or fragmentation at 433 K . This could possibly explain why the experimental IP and AE values are somewhat lower than the M06-calculated values at 298 K .²³

It has been postulated that previous photoionization experiments on vaporized ILs have been unable to detect the intact ion pair because the IP of the ion pair and the AE of the cation (corresponding to the energy of the separated cation and radical, $\text{C}^+\text{A}^\bullet \rightarrow \text{C}^+ + \text{A}^\bullet$) have similar energies and that the ionized ion pair may dissociate on a time scale much faster than that of the ion's residence time in the high-field acceleration region of the TOFMS.²⁴ For the case of $\text{BMIM}^+\text{TCM}^-$, it is important to note that the experimental AE of the cation is at least 300 meV higher in energy than the IP for the ion pair. This energy difference could mean that the lifetime of the ionized ion pair is long enough relative to the time scale of ion acceleration in the TOF mass spectrometer so that it is readily

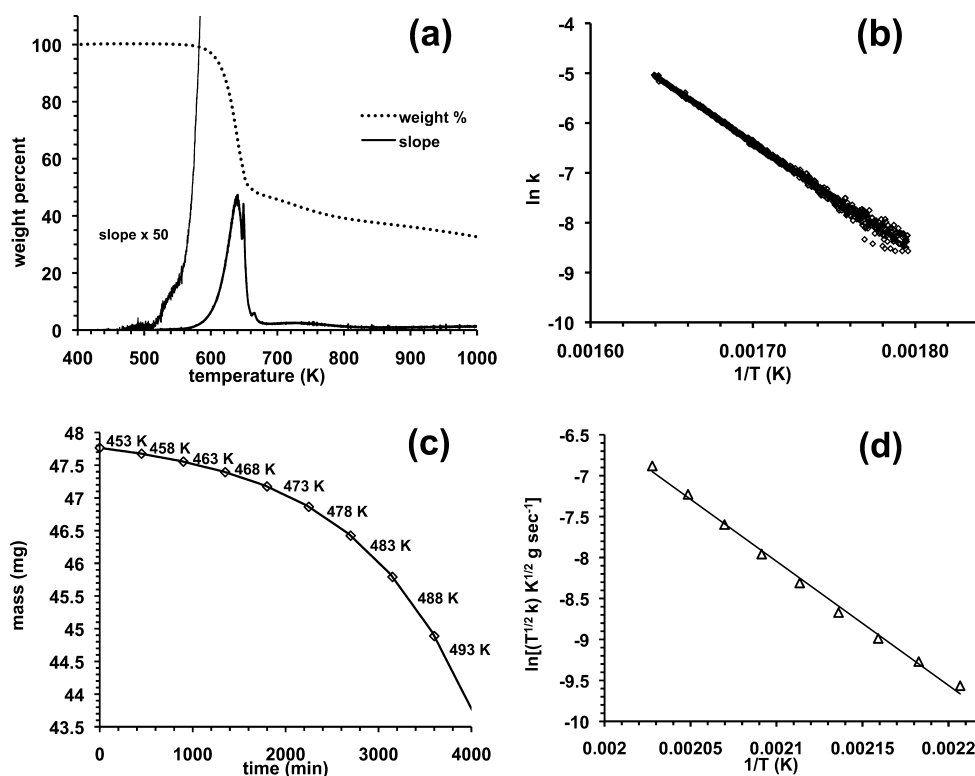


Figure 2. (a) Nonisothermal gravimetric analysis (TGA) of BMIM⁺TCM[−] IL. (b) $\Delta H = 183.0 \pm 4.3$ kJ/mol determined from the slope of the plot for the thermal decomposition of BMIM⁺TCM[−] [data from (a)]. (c) Isothermal gravimetric analysis of BMIM⁺TCM[−] from 453 to 493 at 5 K intervals. (d) $\Delta H_{\text{vap}} = 120 \pm 6.2$ kJ/mol at an average temperature of 473 K, determined from the slope of the plot for vaporization of BMIM⁺TCM[−] [data from (c)]. The 298 K corrected ΔH_{vap} is 143.5 ± 6.2 kJ/mol.

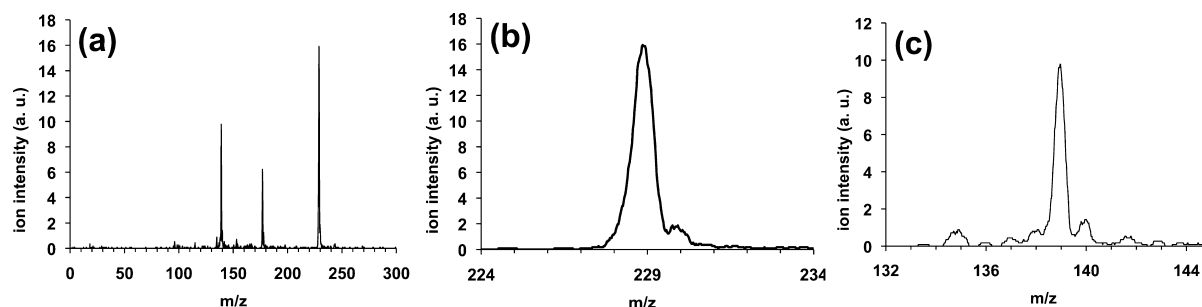


Figure 3. Mass spectra of BMIM⁺TCM[−] at 7.50 eV photon energy, (a) full spectrum, (b) $m/z = 229$ corresponding to the BMIM⁺TCM[−] ion pair, and (c) $m/z = 139$ corresponding to the BMIM⁺ cation. All spectra have been smoothed by 25 points.

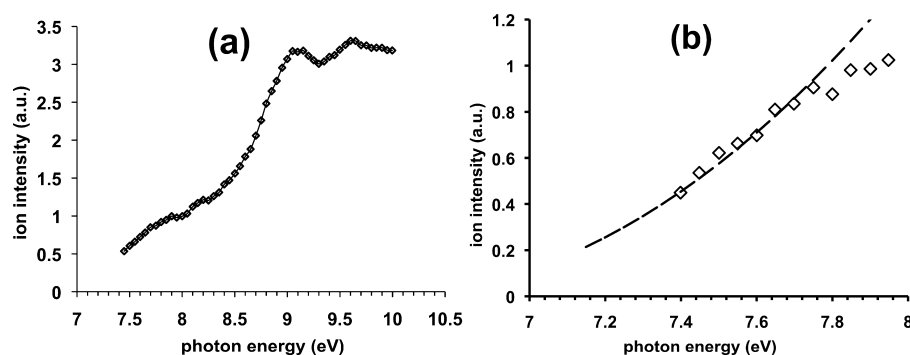


Figure 4. (a) PIE curve for the BMIM⁺TCM[−] ion pair, $m/z = 229$, and (b) enlarged image of (a) near the appearance threshold, where the dashed line indicates the fit to determine the IP.

detected in this experiment. The relatively low temperature of the effusive source required, due to the high vapor pressure of

BMIM⁺TCM[−] relative to that of other ILs, could also help to minimize the internal energy of the vaporized ion pair, aiding in

the detection of its parent photoion. Using Rice–Ramsperger–Kassel–Marcus (RRKM) theory with a tight transition state, the upper limit of the lifetime of the ion pair cation to dissociate to the cation plus radical can be estimated. At 433 K, using ChemRate,²⁵ the density of states of the ground electronic state of the BMIM⁺TCM[•] cation–radical complex is calculated from the vibrational frequencies (scaled by 0.994²⁶) at the M06/6-31+G(d,p) level of theory, and the number of states in the dissociating complex is determined by removing the vibrational frequency corresponding to the dissociation of the complex.²⁷ The calculated lifetimes of the reaction BMIM⁺TCM[•] → BMIM⁺ + TCM[•] as a function of the enthalpy of reaction are shown in Table 1. With a barrier of 300

Table 1. Calculated Lifetimes of the Reaction BMIM⁺TCM[•] → BMIM⁺ + TCM[•] As a Function of the Enthalpy of Reaction (ΔH)

ΔH (kJ/mol)	lifetime (ns)
28.9	1.0
48.2	100

meV, which corresponds to the experimental difference in the ion pair IP and the AE of the cation, the lifetime is 1.0 ns. Due to the large uncertainty in the IP and AE of the cation of 0.5 eV, if a barrier height of 500 meV is used, the lifetime of the cation–radical complex increases to 100 ns. Under our experimental conditions, the time duration of $m/z = 229$ in the acceleration region of the TOFMS is calculated to be 188 ns. The latter $m/z = 229$ lifetime is sufficiently long for the intact cation–radical complex to reach the field-free region in the TOFMS, and thus, the parent ion is detectable. Dissociation of $m/z = 229$ to smaller cationic fragments in the field-free region of the TOFMS could also occur, but these ion fragments would still be detected at nearly the same time-of-flight as the intact ionized ion pair. If fragmentation in the field-free region imparts significant kinetic energy to the ion fragment, peak broadening can occur, but broadening of the $m/z = 229$ peak is not apparent; therefore, either little fragmentation takes place or fragmentation occurs with very little kinetic energy release. In contrast, the 1-ethyl-3-methylimidazolium–NTf₂[•] cation–radical complex, as well as other aprotic ILs, may not have such a large barrier to dissociation, which would explain why the ion pair was not detected in previous experiments.^{22,24,28}

In evaluating the dissociation energy of the ionized BMIM⁺TCM[•] ion pair, which can be described as an ion–radical complex, BMIM⁺TCM[•], there are dispersion forces that weakly bind the TCM[•] radical to the BMIM⁺ cation, and the dissociation process is endothermic. However, the entropy gained upon dissociation of the cation–radical complex from a single particle to two particles can lower the free energy enough to make this dissociation process exoergic. While the M06-calculated difference between the enthalpy and free energy for the ionization process is small, $\Delta H_{\text{ionization}} = 7.40$ eV, $\Delta G_{\text{ionization}} = 7.34$ eV, the difference between the enthalpy and free energy in the DI of the cation–radical process is large (0.62 eV), $\Delta H_{\text{DI}} = 7.49$ eV, $\Delta G_{\text{DI}} = 6.91$ eV, indicating that the dissociation is an entropy-driven process. Calculation of the free-energy profile of the cation–radical dissociation is beyond the scope of this Letter, but it could be possible that, due to competition between energetic and entropic effects, there exists a barrier on the free-energy coordinate that leads to dissociation. This barrier might be large enough to keep the cation–radical

complex intact long enough for it to be detected in the VUV-TOFMS experiment. For other aprotic IL systems, this free-energy barrier may not be sufficiently high for the cation–radical to exist long enough to be measured experimentally, which would explain why their ion pairs have not been detectable experimentally.

We have presented the first measured PIE curve of an intact ion pair of the vaporized IL BMIM⁺TCM[•], which has an estimated RRKM lifetime of the ionized ion pair of up to 100 ns. Dissociation of the ionized ion pair is dominated by the entropic contributions. Experimental determination that the enthalpy of activation for thermal decomposition is substantially higher than the enthalpy of vaporization for this IL provides further evidence that vaporization is the dominant mechanism under VUV PI-TOFMS experimental conditions.

EXPERIMENTAL SECTION

The present experimental PIE measurement setup is a modification of a setup used previously.^{5,11,22,24,28} It uses a new, smaller effusive IL source that is mounted directly onto the repeller plate of the mass spectrometer ion optics; a pinhole in the repeller plate introduces the IL vapor into the ionization region (Figure 1).²⁹ This new configuration increases the IL vapor number density in the ionization region by approximately 250 times versus the previous setup. The IL source was maintained at 433 K, which is significantly lower than the thermal decomposition temperature for BMIM⁺TCM[•], which is ~513 K as measured by nonisothermal gravimetric analysis, or the temperatures used (>573 K) in the previous study where ion pairs were detected.¹⁸ The IL sample (purchased from EMD, purity = 99.8%, HPLC) was loaded into the source, mounted into the vacuum chamber, pumped to <10^{−7} Torr, and degassed for 12 h at 298 K, prior to carrying out any photoionization measurements. The PIE measurements were carried out between 7.4 and 10.0 eV in 0.050 eV steps and co-added for every 500 000 pulses (the VUV line width was 0.023 eV, fwhm). The PIE spectra were normalized for photon flux at each photon energy. Nonisothermal gravimetric analysis was performed on a TA Instruments 2050 using approximately 5 mg of the IL sample, heated at 10 K/min from 323 to 1073 K under N₂. The thermal decomposition temperature was determined by the temperature where a nonzero slope of the nonisothermal gravimetric analysis curve was detected. In a separate isothermal gravimetric analysis experiment, approximately 40 mg of the IL was heated from 453 to 493 K in 5 K steps, and the temperature was held constant at each step for 450 min. DFT single-point energy calculations were performed at the M06/6-31+G(d,p) level of theory (298 K, ZPVE corrected) using the Gaussian 09 suite of programs,³⁰ unless otherwise noted, and the IPs and photoion AEs are reported as ΔG values. The geometry of the BMIM⁺TCM[•] ion pair was taken from ref 19.

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Notes

The authors declare no competing financial interest.

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